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Andrew Byro

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Property Enhancements of Dielectric Nanoparticles via Surface Functionalization

by

Andrew Helmuth Byro

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

2014
This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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Abstract

PROPERTY ENHANCEMENTS OF DIELECTRIC NANOPARTICLES VIA SURFACE FUNCTIONALIZATION

by

Andrew Helmut Byro

Advisor: Professor Stephen O'Brien

This thesis describes the surface modification of barium strontium titanate nanoparticles for use in polymer/ceramic composite thin film capacitors with resultant improved dielectric and film-making properties. Phosphonic acid-type ligands proved to be most effective for surface conjugation to the surface of the barium strontium titanate nanoparticles. Amine-terminated ligands proved to be effective at removing surface adsorbed water before being almost entirely removed during the sample washing stage. Carboxylic acid terminated ligands proved to adhere less well to the nanoparticle than the phosphonic acid, but resulted in thin films with a higher dielectric constant, which was more stable in the measured frequency range than the phosphonic acid. This is seen via a systematic change in thin film variables, including ligand length, ligand reactive head, presence of polymer composite, and concentration of ligand. The nanoparticles were synthesized, ligands attached, then a series of thin film capacitors were fabricated to study the change in dielectric properties. The results show a stabilized dielectric constant over a wide frequency range, a dramatically decreased loss, and better film-making properties. The new materials presented in this study are potentially useful as dielectrics for low-energy-density/low-loss capacitors.
This dissertation is dedicated to my wife Joanna for her patience, love, and support during my PhD. And to absent friends...
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Chapter 1

Introduction

1.1 Capacitors & Capacitance

Capacitors are discrete electronic components used in almost every electronic device on the market. In 2010 alone, the market for capacitors was an estimated $15.1 billion, with nearly 1.3 trillion capacitors sold.\(^1\)\(^2\) In 2008, 1.2 trillion multilayered ceramic capacitors were sold, accounting for close to half of all passive electronic components sold worldwide. While Moore’s Law was stated almost 50 years ago in 1965, the last decade in particular has been a drive in technology towards constant miniaturization of electronics, while maintaining or expanding their capabilities. This is especially apparent in cameras, cellular phones, tablet computers, and other hand-held devices which may have hundreds of capacitors installed per device.

Multilayer ceramic capacitors (MLCCs) are a workhorse of the capacitor industry, and account for close to half of all passive electronic components sold worldwide (electrolytics account for the majority of the other market segment). The reason for the popularity in MLCCs is threefold: they can be surface mounted, they have very high capacitance ratings at extremely small sizes, and manufacturers can simply stack more layers on top of the MLCC in order to increase the capacitance while maintaining the same or even shrinking the footprint. MLCCs consist of stacks of barium titanate ceramic films, separated by thin metal films to act as electrodes.\(^3\)^\(^-\)\(^6\) Barium titanate is most commonly used due to its perovskite structure granting it a strong innate dipole, along with the robustness associated with ceramics.
Barium titanate is both cheap and in ready supply at high purities, and extensive work has been done to characterize the compound. At room temperature the crystalline lattice is deformed along the <1 0 0> plane (Figure 1.1), which leads to the tetragonal conformation. The tetragonal conformation has an innate dipole and can be spontaneously polarized by an external electrical field. As a result, the material has a high dielectric constant, and is excellent for use in ceramic capacitors.

Capacitance is the capacity of a material, called an insulator or a dielectric, to hold an electrical charge. Any material capable of holding an electrical charge can be considered a form of capacitor. This thesis focuses on the parallel plate capacitor. In a parallel plate capacitor, a dielectric film is sandwiched between a pair of electrodes. In an ideal capacitor, the capacitance is the quotient between the charges on the plates (given by +Q and −Q), and the strength of the applied field (voltage, V), or:

\[ C = \frac{Q}{V} \quad (1.1) \]

where C is defined as capacitance, and has the units of 1 Coulomb/1 Volt = 1 Farad (F).
1.2. Parallel Plate Capacitors

Capacitance in a parallel plate capacitor is measured via Equation 1.2. $C$ is the capacitance measured, $t$ the thickness of the dielectric, $A$ the area of the capacitor, and $\varepsilon_0$ is the permittivity of vacuum, and $k$ is the measure of the characteristic polarizability of a given dielectric, also known as the dielectric constant.

$$C = \frac{A\varepsilon_0 k}{t} \quad (1.2)$$

Dielectric materials are electrical insulators whose dipoles are induced to align (or polarize) via an external electrical field against incoming electrons. Energy is expended in polarizing and maintaining the polarization of the dipoles of the insulating material. The more insulating the material, the less energy is lost in maintaining the polarization, so that more charge can be placed in the plates with the same voltage.

It is advantageous to increase the capacitance of the dielectric films, as this allows for the creation of physically smaller capacitors with the same capacitance properties as larger capacitors. However, on examination of equation 1.2, capacitance increase is limited to changes in either the geometry or the dielectric constant. Equation 1.2, however, does not tell the whole story. The energy stored in a parallel plate capacitor within an electric field may be expressed as:

$$E = \frac{1}{2CV^2} \quad (1.3)$$
Extending Equation 1.3 to its boundaries, it can be seen that the maximum amount of energy \((E_{\text{max}})\) capable of being stored in a capacitor depends on the maximum applicable voltage without reaching dielectric breakdown voltage \((V_B)\).

\[
E_{\text{max}} = \frac{1}{2CV_B^2} \quad (1.4)
\]

The maximum energy density \((D_{\text{max}})\) can also be derived from Equation 1.4:

\[
D_{\text{max}} = \frac{E_{\text{max}}}{\text{vol}} = \frac{(\frac{1}{2})CV_B^2}{A\times t} = \left(\frac{1}{2}\right) \varepsilon_0 k \left(\frac{V_B}{t}\right)^2 = \left(\frac{1}{2}\right) \varepsilon_0 k E_B^2 \quad (1.5)
\]

where \(E_B\) is the dielectric breakdown field strength. Therefore, the maximum energy density \((D_{\text{max}})\) is proportional to both the permittivity of the dielectric material \((k)\) and the square of the dielectric breakdown field strength.35

1.3 Capacitors in AC Circuitry

Ohm’s Law states that in a DC circuit, the current through a conductor between a pair of points is equal to the quotient of the voltage applied across the conductor to the resistance of the conductor to the flow of electrons, or

\[
I = \frac{V}{R} \quad (1.6)
\]

In AC circuitry, it is necessary to introduce the concept of impedance \((Z)\) to account for the mechanisms which impede the flow of current in addition to the normal resistance found in DC circuits. Impedance is a complex number derived from both real (resistance, \(R\)) and
imaginary (reactance, X) components. The reactance is the opposition of a capacitor to a change in voltage, while the resistance is the opposition of a capacitor to current. If Ohm’s Law is read as the voltage-current ratio for resistance, then the impedance is the voltage-current ratio at a particular frequency.

\[ V = I|Z| \quad (1.7) \]

Impedance can then be described as follows:

\[ Z = R + jX \quad (1.8) \]

where, \( j \) is the imaginary constant and replaces the more usual \( i \) to prevent confusion with the symbol for current. The method by which impedance is determined in dielectric spectroscopy will be discussed in greater detail in Appendix A.

While an ideal capacitor stores and releases energy with 100% efficiency, real capacitors carry imperfections which create resistance. This resistance is known as the Equivalent Series Resistance (ESR), and can be modeled to a reasonably accurate degree according to the lumped element model by approximating an ideal capacitor in series with a resistor.

In general, the ESR represents dielectric loss in a capacitor, taking into account both the loss due to the dielectric’s conduction electrons and the energy of polarization of the dipoles within the capacitor. Leakage, however, is distinct from ESR, and comes from the dielectric material not
being a perfect insulator, leading to a slow leakage of electrons through the capacitor over time, resulting in a gradual loss of energy from a charged capacitor over time.

Figure 1.3 shows delta as the angle between the resistance and the reactance. Taking the tangent of delta gives the Dissipation Factor (DF), or:

$$\tan(\delta) = \frac{E_{SR}}{|X_c|} = DF \quad (1.9)$$

The DF is a measure of the rate of loss of energy in a capacitor, and is usually measured concurrently with capacitance measurements. In summary, the capacitance describes the energy stored in a capacitor, while the DF describes the efficiency of using the capacitor.

1.4 Types of Polarization

There are four major microscopic mechanisms by which dielectric polarizations occur: electron polarization, vibrational polarization, dipolar polarization, and translational polarization. These mechanisms are depicted below in Figure 1.4.

Electron polarization occurs when the electron cloud of a neutral atom within the dielectric material is deformed via an external electrical field. It is impermanent, and dissipates upon removal of the applied electrical field.

Vibrational polarization stems from atomic displacement separating charges. This is generally found in ionic substances where the applied electrical field shifts the relative positions of the positive and negative ions, and is also impermanent.
Dipolar (also known as Ionic, or Rotational) polarization is found in particular ferroelectric materials, and results in a permanent dipole – a remnant dipole after removal of the applied field. These materials are unit cells, molecular segments, and domains possessing an innate dipole moment even without the presence of an applied field. When in the presence of an electrical field, the dipoles orient along the direction of the field so that the net dipole moment is non-zero.
Translational polarization is usually associated with the presence of migrating charges over macroscopic distances. The charges tend to be trapped and accumulate at physical barriers such as defects, phase boundaries, or impurities, and at the electrode, where the materials are conductive. Accumulated charges distort the local electric field and result in changes in the permittivity of the material. Translational polarization is particularly found in multiphase systems such as polymer-ceramic nanocomposites.

At higher frequencies (~1GHz and above), the most significant contribution to the relative polarization is atomic and electronic polarization, both of which are fairly weak. However, our interest lies in the lower frequency range, where the most significant contribution to the polarization comes from dipolar relaxation. For this reason, our interest lies in enhancing the dipolar polarization of the thin film capacitor.

1.5 Barium Strontium Titanate Nanoparticles.

Barium titanate $\text{BaTiO}_3$ (Figure 1.5) is a perovskite-structured ceramic material commonly used as the dielectric material in commercial ceramic capacitors. Its popularity stems from a strong innate dipole which spontaneously arises within the unit cell itself at room temperature, which is usable over a wide range of AC frequencies. In addition, it has an inexpensive price, well characterized properties, and long-term aging and thermal stability.

This stands in marked contrast to classical electrolytic capacitors which, while cheap, are bulky, rely on an electrolyte solution which can dry out over time, are more prone to catastrophic failure. In turn, metal oxide perovskites generally require high temperature processing, a low
dielectric strength (the amount of voltage which can be applied before burning out the dielectric), and high leakage.

Figure 1.5. Perovskite barium titanate unit cells. Left: Cubic phase, with no innate dipole. Right: tetragonal phase. The innate dipole aligns with the external electrical field, and maintains the distortion even after removal of the external field (spontaneous polarization). If the electrical field is re-applied and moved, the alignment follows the field. While the polarization is usually depicted as solely a shift in the central titanium, there is actually a concerted movement of ions, including the oxygens surrounding the titanium which shift slightly around the titanium.

Our lab has previously published experiments in synthesizing barium strontium titanate nanoparticles\textsuperscript{83}, changing the barium/strontium ratio to study the dielectric effects. Strontium titanate, while maintaining the same tetragonal perovskite structure as barium titanate, is nonetheless paraelectric, with a smaller unit cell, while barium titanate is ferroelectric. In effect, the internal dipole of a paraelectric compound will return to its original position upon removal of an external electrical field, while a ferroelectric will maintain the oriented dipole\textsuperscript{20,85-93}. But ferroelectricity is a cooperative phenomenon which deviates from bulk behavior as the number of unit cells decreases. This is in turn further complicated since cubic barium titanate is paraelectric, while tetragonal is ferroelectric.
Barium titanate nanoparticles are rarely all tetragonal or all cubic, instead retaining a tetragonal core with a cubic surface. Changing synthetic parameters (amount of water present, temperature, length of the reaction) affects the ratio of the core volume to the surface volume.\textsuperscript{94-96} The critical lower size limit beyond which spontaneous polarization is no longer observed is referred to as the superparaelectric limit. By making nanoparticles from both barium and strontium, our lab (the O’Brien group) achieved a synergistic effect in the properties, fabricating nanoparticle-based capacitors at or near the superparaelectric limit.

### 1.6 Curie Temperature

The Curie Temperature is the temperature where a material’s spontaneous polarization changes to induced polarization, or vice versa. To put it another way, it is the temperature at which the aligned electric dipoles within a material change direction. When discussing barium titanate, it is generally the temperature at which the unit cell undergoes a phase transition from tetrahedral to cubic (or vice versa), with a corresponding loss of internal dipole (see Figure 1.6).

Figure 1.6. Change in relative permittivity of bulk barium titanate depending on temperature. Peaks in permittivity mark the various Curie temperatures which separate the different crystalline phases noted in their respective temperature ranges. Barium titanate nanoparticles exhibit significantly depressed Curie temperatures.
Until fairly recently,\textsuperscript{97} the Curie temperature was assumed to significantly decrease once the diameter of the barium titanate nanoparticle dropped below $\sim 100$ nm. Ohno et.al.\textsuperscript{30} recently observed that on refluxing barium titanate nanoparticles in dimethylformamide, both surface adsorbed water molecules, and water molecules which were found within the crystal lattice of the nanoparticle (vestiges of the synthetic process used to synthesize the nanoparticles) were both removed.\textsuperscript{30,97} The result was a Curie temperature which was not significantly depressed until a particle diameter of $\sim 40$ nm. By $\sim 20$ nm diameter, the Curie temperature had reached room temperature. This is significant because as seen in Figure 1.5, the greatest relative permittivity may be found in the region of the Curie temperature, rather than being found exclusively in tetragonal or cubic phases.

1.7 Dielectric Particle-Polymer Composites

A composite material is a mixture of two or more components which behave like a single material with a fusion of properties from the different components. This has led to mixing of high permittivity polymers\textsuperscript{98-130} with high permittivity dielectric particles, making high permittivity, low leakage, high dielectric breakdown strength, easily processable films\textsuperscript{131-182}. There are a number of different configurations of composites, according to a system developed by Newnham, et. al\textsuperscript{183} (see Figure 1.7).

The dielectric constant of a host-polymer and filler-particle composite film is not easily calculated. A multiphase system must take into account interactions both between the polymer and the particle as well as between particle and particle. When particles are plated with no polymer matrix, the particle-to-particle contact is maximized. As the particle-to-particle contact
increases, the space between particles decreases. It also decreases the likelihood of an electron percolating its way from one electrode to the other.

However, with spherical particles, a great deal of empty (void or interstitial) space still exists between the particles. This in turn means that the films must be thicker in order to prevent
electron migration. The maximum packing density of spheres is \(~74\%\) which still leaves a quarter of the volume empty, unless something else (polymer matrices, ligands, smaller particles) fills that space.

Analytical theories describing the effective dielectric constant have evolved, particularly in regards to 3-0 composite systems. These theories predict an effective permittivity increase either by increasing the volume fraction of the particle fillers, or by increasing the permittivity of the polymer host.

The dielectric constant of the film is sensitive to the quality - even a single pinhole in the film can significantly decrease the overall dielectric capabilities of the film (Figure 1.8 B). This can be demonstrated by considering the Kerner Model\(^{184}\):

\[
\varepsilon_{\text{eff}} = \frac{\varepsilon_h f_h + \varepsilon_f f_f}{f_h + f_f} \left( \frac{E_{fz}}{E_{hz}} \right) (1.10)
\]

The Kerner model is a simple composite medium theory. It treats the dielectric filler particles as polarizable spheres in which dipoles are induced under an applied electric field. The effect of the host material on the electric field within the particles is taken into account, but the effect of the particles on the electric field of the host is ignored. The effective permittivity ($\varepsilon_{\text{eff}}$) is calculated by averaging the permittivities of both the host ($\varepsilon_h$) and the filler ($\varepsilon_f$) particles, each adjusted by the volume fraction ($f_h$, $f_f$) and electric field ($E_{fz}$, $E_{hz}$) in each component. This model, while very good for prediction of dielectric properties of composites at low filler volume fractions ($\leq 20\%$), loses accuracy at higher volume fractions. This is because the model does not
take into account either particle-particle dipole interactions, or their effect on the surrounding medium. The error this introduces becomes more pronounced at higher volume fractions. To better explain higher volume fraction fillers, Jayasundere and Smith\textsuperscript{185} and others\textsuperscript{185b} modified the Kerner model to account for dipolar interactions between pairs of neighboring spherical filler particles, which leads to a modified local field in the medium, which results in the following equation:

$$\varepsilon_{\text{eff}} = \varepsilon_{hf} + \varepsilon_{ff}(A)(B)$$ \hspace{1cm} (1.11)

$$A = \frac{3\varepsilon_h - \varepsilon_{ff}}{\varepsilon_f + 2\varepsilon_h} \hspace{1cm} B = 1 + \frac{3f_f(\varepsilon_f - \varepsilon_h)}{\varepsilon_f + 2\varepsilon_h}$$

This model, however, assumes only a two-phase system. In reality, imperfect films may result in the presence of holes, voids, or interstitial spaces. To address this, a three-phase model\textsuperscript{186,187} may be used instead:

$$\varepsilon_{\text{eff}} = \varepsilon_h + f_v(\varepsilon_v - \varepsilon_h)a_v + f_f(\varepsilon_f - \varepsilon_h)a_f$$ \hspace{1cm} (1.12)

$$a_r = 1 - s[(\varepsilon_r - \varepsilon_{\text{eff}})^{-1} \varepsilon_{\text{eff}} + s]^{-1} \text{ and } r = v, f$$

where $a_r$ is the electric field concentration factor for corresponding $r$ phases (void and filler), $\varepsilon_v$ and $f_v$ are the dielectric constant and volume fraction of the void respectively, and $s$ is the depolarization factor ($1/3$ for spherical particles). As equation 1.12 is recursive, $\varepsilon_{\text{eff}}$ is evaluated while setting the dielectric constants of void constant, varying the dielectric constant of the host polymer, volume fraction of filler, and volume fraction of the void, and slowly decreasing the volume fraction of the particle filler (Figure 1.8).
What is so particularly important about these equations is that they allow the prediction and calculation of the effects of the permittivities of various mixtures. For example, depending on the volume fraction, the permittivity of the particles can be incredibly high, but the permittivity of the film as a whole is still low. This means that the parameters of the film may be adjusted to result in the maximized overall quality, especially over higher frequencies.

Suspension of the nanoparticle in a polymer matrix is a popular method to enhance dielectric values. The nanoparticles are suspended in a high-k polymer which is then cast into a film. While some compounds in the right ratios can lead to an enhancement of the overall dielectric of the film as the sum of the dielectric constant of both the nanoparticles and the polymer host, this is rare. One important consideration when using this method is that the ratio of nanoparticle-to-polymer must be adjusted and measured. Too much polymer and the advantages

![Figure 1.8](image-url)
of having nanoparticles in the film are lost, due to the large areas between the nanoparticles filled with low dielectric constant polymer. Using too little polymer leads to the particles not being fully suspended in the polymer, leading to inconsistent, non-uniform films. Kim, et. al. found that the highest dielectric constant thin film was attained with a ratio of 60% nanoparticle and 40% polymer.\textsuperscript{186} However, the dielectric loss was also fairly high, which also showed in a fairly rapid decrease in the dielectric constant of the thin film as the frequency was increased. When the ratio was changed to 80% nanoparticle and 20% polymer, the overall dielectric constant was half of the 60% nanoparticle sample, but was much more stable up to 1 MHz, as well as have a very low dielectric loss. This ratio will need to be altered depending on the particle size, as the exposed surface area, as well as the overall density of the nanoparticles will change as they increase or decrease in size.

Use of a polymer matrix has its own drawbacks. Suspending the nanoparticles in polymer can reduce the flexibility of the overall film. Many of the polymers which have high dielectric constants are inappropriate to use because they do not react well to the strain of bending and flexing, and therefore the properties are not repeatable, which limits their use for components. Or they may require a certain amount of very careful, specific mechanical manipulation to assume the particularly desired phase. The use of the polymer can also severely reduce the effective temperatures that the thin film can be used in, as the ceramic nanoparticles themselves can respond well to very high temperatures, but the polymer matrix will melt (typically >100-200 °C) and eventually break down generally within a few hundred degrees.

The polymer matrix can also potentially limit the methods available for thin film formation. For example, printing speed, precision, and volume can be decreased significantly by an increased viscosity of the sample. While not impossible, it may require more specialized
equipment to create the thin films, and decrease the overall production speed and capability because of this. It can also greatly increase the cost of manufacture of the film, depending on the type and purity of the polymer used.

Finally, significant problems exist ensuring quality control during thin film formation. The reason for this is the difficulty associated in creating absolutely perfect layer stacking of the nanoparticles. The discontinuities in the stacking lead to non-idealized distribution of the overall dipole when influenced by an electric field. The most common solution to this problem has been to suspend the nanoparticles in a polymer, then cast the mixture as a film. However, as previously discussed, this is not always available as a solution.

1.6 The Surface of BST

In an effort to increase the distribution properties of the nanoparticles within the polymer matrix, researchers have mainly focused on methods by which the hydroxyl group on the surface of the nanoparticle can be conjugated.\textsuperscript{188-196} Alternately, if the nanoparticle lacks surface hydroxyl groups, they have investigated how to attach and then functionalize them.\textsuperscript{94,197, 198} While there are a large variety of compounds used as surface modification agents, the active sites tend to be variants on organic acids. Examples of these active sites are phosphonic acid and sodium acetate. These compounds are popular due to the ease with which they can react with the surface hydroxyl groups, rather than how well they coordinate to the surface of the nanoparticle itself.

By functionalizing the surface of the nanoparticle with an appropriate ligand, one can tune the physical properties of the nanoparticle, as well as that of the film formed. Our lab has
worked with barium strontium titanate nanoparticles, in an effort to enhance the dielectric constant of the films created. The unit cell shows that there are plenty of functionalization sites on the surface of the nanoparticle. Due to the hydrothermal synthetic method used, these sites are already filled with hydroxyl groups. These hydroxyl groups are partially responsible for the structure, growth, and particle-particle associations of the nanoparticles.98,199, 200

However, thermogravimetric analysis (TGA) of the bare nanoparticles shows that ~51% of the available surface sites are already hydroxylated, which should suffice to allow observation of any significant changes without going through the added time and expense of further hydroxylation.

Running TGA on the surface of BST, we can observe a change in weight of 1.92% in the surface hydroxyl group region (370-480 °C). This corresponds to roughly 51% of available surface sites being filled with hydroxyl groups. These hydroxyl groups offer a platform for surface treatments. Rather than attempting to coordinate a ligand directly with the surface of the nanoparticle it can instead react with the surface hydroxyl groups to form a stable layer.

Our interest lies in removal of surface water, so coordinating to those hydroxyl groups should prove sufficient to see a significant decrease in dielectric loss without requiring an intermediate surface hydroxylation process required by other methodologies.
A series of three different coordination heads will be tested to find which reacts with the surface best. Each compound will also have a polytetrafluoroethylene (PTFE) tail. PTFE has well-known and defined dielectric properties in bulk medium, and is generally seen as very poor (the $k$ value is roughly 2). This is because in long chain form, the molecule will twist into a helical conformation to minimize strain on the molecule, reducing the overall dipole.\textsuperscript{54-56} However, we will be studying compounds with short chains of known length, and varying that length. The aim is not so much to enhance the dipole of the overall film, but rather to improve the particle-particle interactions to create a better film. The surface ligands being longer than hydroxyl groups will help fill the interstitial spaces between the nanoparticles.

![Figure 1.10. Representation of various surface functionalities of the oxide nanoparticle.](image)

Describing the surface of the oxide as a uniform monolayer coating of single-species hydroxyl groups is incorrect. In fact, the surface is a complex territory of various oxidative states, leading to an acidic surface (either Lewis or Bronsted, Lewis generally found in pure oxides, Bronsted generally found in mixed oxides). The different surface hydroxyl species allow further functionalization via either hydrogen bonding or acid-base reaction. In addition, however, there is a further layer of water, generally several layers thick, which is hydrogen bonded to the surface hydroxyl groups.
Because the surface hydroxyl groups may either hydrogen bond or acid-base react, although reactive ligands are usually acidic, mildly basic amine-terminated ligands were chosen as variable ligands. The amine terminal group would have the capability to either hydrogen bond...
with the surface hydroxyl groups, or occasionally perform an acid-base reaction, depending on the surface hydroxyl group available.

The ligands will be sorted according to the head group which attaches to the particle. These are primary amines, carboxylic acids, and phosphonic acids. The lengths of these compounds (the number of carbons forming the chain) will be varied to examine any effect that ligand length may have (see Table 2.1). These compounds are all readily available from commercial sources.

Several proposed reaction mechanisms are shown in Figure 1.11.

Ultimately, the nanoparticles must be formed into thin films. High quality thin films of BaSrTiO₃ nanoparticles have been successfully produced in the past via spin-coating. For this series of experiments, films will initially be created under the same conditions as used to create BaSrTiO₃ thin films. Film quality will be assessed via SEM to check for thickness, clumping, aggregation, pinholes, gaps, or other significant defects. The spin coating conditions (RPM, solvent, number of coats, time for each coat to dry) will be adjusted depending on the observed film defects. The films will also be examined for changes to the overall film structure; whether the association between the nanoparticles has visibly changed, i.e. the packing structure.

The ligand length should play a large part in any changes to the interparticle interaction and stacking. The thin films will then be tested for their capacitance properties.
1.6 Outline of Dissertation

This dissertation is outlined as follows.

Chapter 2 will discuss the synthesis and select characteristics of barium strontium titanate nanoparticles. It will describe in detail the nanoparticle synthesis used for this thesis, as well as the morphological characterization of the nanoparticles. Chapter 2 will then begin to discuss several different choices for polymer matrix, then move on to a discussion of the controlled ligand functionalization of the nanoparticles. The functionalization reaction here will be elucidated.

Chapter 3 will show the results of the experiments detailed in Chapter 2, and discuss the observations.

Chapter 4 concludes the thesis, with suggestions for future research related to applications of the discussed processes.

Appendix A discusses the fabrication and testing of capacitor devices. Here will be discussed the manufacturing requirements of parallel plate capacitors, and the steps which were taken to fulfill those requirements. Further discussion will focus on preparation of the thin film dielectric, and then the theory and practice of measuring a thin film capacitor via dielectric spectroscopy.

Appendix B will discuss additional work done tangential to the functionalization work. This will include discussions regarding the design and setup of custom instrumentation and software implementation, as well as animations created for presentation at the ARPAE 2012 meeting in Washington, D.C.
Chapter 2

Synthesis of Nanoparticles and Ligand Reactions

In Chapter 1, barium strontium titanate nanoparticles (BST) and ligand functionalization were introduced. This chapter will describe details of the materials used and the synthetic processes necessary to create a ligand functionalized BST nanoparticle-based thin film. All BST nanoparticles used for this thesis were synthesized in-house via the solvothermal processes.

This chapter will be broken into the following parts:

2.1 Solvothermal synthesis of BST nanoparticles.

2.2 Discussion of polymer matrices.

2.3 Ligand choices and reaction mechanisms.

2.1 Solvothermal Synthesis of Barium Strontium Titanate Nanoparticles.

As mentioned in Chapter 1, BT has proven to have both high dielectric values and dielectric strengths, as well as being both inexpensive and readily available. It is for these reasons that it is one of the more popular materials used in capacitor manufacture.
Figure 2.1. Reaction scheme of solvothermal synthesis of barium titanate.

4.9 mmol Ba(OAc)₂

2.1 mmol Sr(OAc)₂

5 mL water

Stir until dissolved

5 mL water

Stir 2 min

Stir 5 min

Stir 30 min

Transfer to autoclave cylinder, heat 75 °C 15 hours

60 mL ethanol

6.7 mL Ti(iPr)₄

Dropwise add'n

1 g NaOH

2 mL water

Dropwise add'n

Centrifuge, wash, sonicate x 3

Figure 2.1. Reaction scheme of solvothermal synthesis of barium titanate.
The solvothermal BST synthesis (Figure 2.1) was first developed by O'Brien et. al. The solvothermal synthesis utilizes alcoholysis between a metal-organic precursor and an alcohol. It requires neither organic surfactants nor unusually high temperatures.

All materials were ordered from Sigma-Aldrich and used without further purification. To a flask was added 4.9 mmol barium acetate, 2.1 mmol strontium acetate, and 5 mL 18.2 MΩ water. The flask was stirred until the contents had fully dissolved. In a separate flask was added 60 mL 200 proof degassed ethanol and 6.7 mmol titanium isopropoxide. This was stirred for 2 minutes. The barium/strontium solution was added to the titanium isopropoxide solution dropwise, whereupon it turned a thick cloudy white, followed by 5 minutes of stirring. To this was added 2 mL of 12.5 M sodium hydroxide solution in 18.2 MΩ water dropwise to neutralize the sample, followed by 30 minutes of stirring. The sample was then transferred to an autoclave cylinder and heated at 75 °C for 15 hours, followed by washing the sample three times with ethanol.

The result is a highly crystalline, monodisperse barium titanate, free of contamination from typical contaminants such as barium carbonate. Moreover, the diameter of the resultant nanoparticles can be controlled via control of water content during synthesis. The reaction
scheme is clearly illustrated in Figure 2.1, and the resultant nanoparticles may be seen in Figure 2.2.

Solvothermal synthesis results in a number of advantages over conventional hydrothermal synthesis. Barium titanate is known to be thermodynamically unstable in aqueous solution because $\text{Ba}^{2+}$ ions leach from the particle surface. This causes a deviation in the stoichiometry, and a degradation of the dielectric properties due to changes in the crystal structure. The 15 hour reaction time is key, as crystallization of barium titanate is dominated by kinetics at low temperature and short reaction times, but thermal equilibrium becomes more dominant at higher temperatures and longer reaction times. It is in the kinetics stage that the meta-stable cubic barium titanate is crystallized, and lattice defects in the form of hydroxyl ions and their compensated cation cavities are formed. Thus, cubic barium titanate with some tetragonality is found over long reaction times/high temperatures by reducing the point defects in the particles.$^{38}$

2.2 Polymer Matrices

When examining the literature for particle-polymer dielectric composites, the most commonly found polymer is polyvinylidifluoride (PVDF), and with good reason. With its repeating $-\text{CF}_2-\text{CH}_2-$ structure, PVDF has an extremely high dielectric constant due to the $-\text{CH}_2-$ allowing the fluorines (and more importantly, the dipoles from the fluorines) of the $-\text{CF}_2-$ to align en masse to have an enormous overall molecular dipole. However, pure PVDF is impractical for use as a nanoparticle composite, due to the necessary work required to force the PVDF chain into the desired configuration. Instead, researchers generally work with one of
several PVDF co-polymers (such as PVDF-HFP, PVDF-TrFE), which offer dielectric constants which are still lower than PVDF, yet much more processable.

In contrast, our lab initially successfully experimented with using Parylene C polymer as a film enhancer/sealer. As a film enhancer, Parylene C would fill any pinholes in the film and potentially smoothen the surface, enhancing the dielectric. As a sealer, it would effectively act to protect the nanoparticle thin film from the environment. However, Parylene C is applied to surfaces via condensation from the vapor phase, meaning that while it can coat the surface of the nanoparticle film, and partially penetrate the exposed surface of the film, it is incapable of fully penetrating the film. This meant that there was still a great deal of void space left in the interstitial spacing between nanoparticles below the surface.

To address this issue, we experimented with polyvinylpyrrolidone (PVP) as a polymer matrix\textsuperscript{187,201}, which offers several advantages over PVDF co-polymers, even though it has a lower dielectric value. PVP may be purchased in powdered monomer form as N-vinylpyrrolidone. While the monomer is dissolved into a polar solvent, it remains stable and non-polymerized until it is spin-coated, which means that the polymer matrix forms around the suspended nanoparticles, rather than attempting to force the polymer into an already created film (as with Parylene C) or requiring complicated processes like ball milling in order to ensure a uniform distribution of nanoparticles within the film. This matrix is highly polar, does not require additional heat treatment, is both environmentally friendly and non-toxic, and allows the
added nanoparticles to be suspended while still in solution. This means that the fluid composite may be spin-coated, spray-coated, or printed and will form high quality thin films.

2.3 Surface Ligands

A series of short-chain poly-fluorinated alkanes was prepared for ligandization of the nanoparticles. These compounds (Table 2.1, 2.2) were chosen for several reasons. Each ligand has a distinct head/tail structure, allowing separate evaluation of the effect of both the reactive ligand head and the length of the polyfluorinated tail. All ligands were commercially available and used without further processing.

Polytetrafluoroethylene (PTFE, a.k.a. Teflon®) is known to have a complex structure which has resulted in decades of dispute. What is generally acknowledged is that it is a helical structure between 19 °C-30 °C (phase II) and a slightly different helical structure at 30 °C (phase IV) (-CF2- = 1 unit, unit/turn of 13/6 for phase II and 15/7 for phase IV). The helical structure shapes the molecule into a near-cylinder which stacks and interacts with neighboring PTFE units in complex manners, allowing them to crystallize.

The ligands used were not entirely PTFE, but instead had a reactive head on one end and a -CF3 group on the other end. Nonetheless, the bulk of most of the molecules, and the points of interaction between nanoparticles was PTFE. In all cases, the ligands were shorter than a single helix turn of PTFE.

When the local density is high enough (a hexagonal close-packed structure), PTFE helices begin to interact and influence one another in complex ways. The helices rotate to fit one
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</table>

Table 2.1. List of ligands and select properties. A shorthand naming scheme for each ligand has been adopted. The name begins with a number designating the length of the carbon backbone, followed by PF (for poly-fluorinated), then initials indicating the functional group reactive head (A: amine; CA: carboxylic acid; PA: phosphonic acid).
<table>
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Table 2.2. List of ligands and select properties. A shorthand naming scheme for each ligand has been adopted. The name begins with a number designating the length of the carbon backbone, followed by PF (for poly-fluorinated), then initials indicating the functional group reactive head (A: amine; CA: carboxylic acid; PA: phosphonic acid)
another—in effect acting much like a screw and a threaded bolt. This process is also known to stimulate helix direction reversals when helical left/right conformations are mismatched in order to form greater packing density (see Figure 2.4). The process takes up to 30 milliseconds to occur, fast enough to be a non-issue.

I hypothesized that a combination of factors (the short ligand length, close pack density, heating above the phase transition temperature, then cooling again below it while in close proximity to allow the helix to stretch and release) assuming sufficient packing density of ligands on neighboring NPs would allow complex interactions between the nanoparticles to form sufficient to increase overall film formation quality. As a reminder, the packing density of hydroxide on the nanoparticles is calculated as 51%, as seen in Figure 1.9, so a uniform delocalized distribution of ligands (assuming that every reactive site was reacted with) would be unlikely to form such complicated structures.

However, such interactions would not necessarily require completely uniform coverage, and only a few localized areas of high density would be sufficient to allow the ligands to interact. This localized high density would influence the opposing ligands to reverse conformation to allow the ligands to more easily screw into one another. In addition, perfluoromethyl (-CF3) groups show an inhibiting effect on macroscopic creep, where linearly aligned PTFE chains can translate relative to one another.
2.4  Ligand Functionalization

Surface functionalization reaction was adapted from the method developed by Kim et. al.\textsuperscript{178} To a suspension of nanoparticles in 200 proof ethanol, 0.2 mmol of ligand was added, followed by an hour of refluxing. Experiments comparing reflux times (1-5 hr) displayed no marked change in properties, so data presented here uses samples refluxed for 1 hour as the standard. Reflux was followed by a series of washing steps to remove excess ligand as well as loosely-bound ligands. The sample was initially dissolved in 95/5 ethanol/water.

Not all samples were able to suspend sufficiently in 95/5 ethanol/water in order to be spincoated into thin films. These samples (5PF-A, 7PF-A) showed a heightened viscosity in

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2_4.png}
\caption{PTFE chains assuming the same rotational orientation via localized exposure. This allows for tighter packing density and greater stability. At the same time, closely packed chains tend to screw along the thread created by the fluorines on the surface of the polymer. Above 30° C, the transition from phase II to phase IV results in a slight relaxation of the helical structure (13/6 units/turn to 15/7), here exaggerated for clarity.}
\end{figure}
solution, and may be explained as samples where some of the ligands detached themselves after the particles were washed, but may have continued to associate with the surface of the nanoparticles.

Fluorinated compounds usually require fluorinated solvents in order to properly dissolve. In this case, however, the nanoparticles were able to continue to be suspended, in most cases. This is explained by the incomplete functionalization of the surface hydroxyl groups, which suffice to allow the nanoparticle to remain suspended.

Figure 2.5. Scheme for surface functionalization of barium strontium titanate nanoparticles and subsequent thin film manufacture.
Chapter 3
Results and Analysis

The goal of this study has been to find a ligand or series of ligands which would improve the dielectric properties of BST nanoparticle-based thin film capacitors. This improvement in particular would focus on both a stabilization of the dielectric constant and a decrease in the dielectric loss over a large frequency range. In order to address this, it was decided to tackle the problem of surface water adhering to the nanoparticle.

3.1 Dielectric Spectroscopy

In thin film capacitors made with BST NPs, surface adsorbed water is characterized by a high initial dielectric constant with a rapid decrease in response to increasing frequency. Simultaneously, a very high dielectric loss will also decrease in response to increasing frequency. This is due to contribution from interfacial polarizations and surface absorbed water molecules, whose polarization direction is incapable of keeping up with the frequency switching of the AC electric field. As the frequency increases, the dielectric properties stabilize as the intrinsic dielectric properties of the BST dominate. This is clearly visible in Figure 3.1.

The addition of poly-fluorinated ligands shows a marked difference in dielectric properties. The dramatic drop in dielectric constant below 1 kHz is gone, and the resultant
Figure 3.1. Effective dielectric constants and dielectric losses of ligand-functionalized nanoparticles. Dielectric constant and loss of PVP polymer is included to act as a visual minimum value. Ligand-functionalized samples show improved dielectric characteristics to various extents. Samples A and B represent different volume fractions of nanoparticles (~50% and 70%, respectively. A 60% was also synthesized but not presented here for clarity.)
Dielectric constants are now stable over the frequency range. At the same time, the dielectric loss has also shown to dramatically decrease by nearly an order of magnitude.

Previous observations showed that in the 60-70% nanoparticle volume fraction range, capacitors would show their most intense, but potentially less stable dielectric constant. For this reason, two sets of capacitors were fabricated to determine the preferred volume fraction, each roughly 60% and 70% volume fraction according to the following formulae:

\[ X_f = \frac{(x_1 - \frac{x_1}{4}) - (y_1 - \frac{x_1}{4})}{T_{tot}} \] (3.1)

\[ Y_1 = (T_{tot} - x_1) + \frac{x_1}{4} \] (3.2)

\[ X_f = \frac{2x_1 - \frac{x_1}{4} - T_{tot}}{T_{tot}} \] (3.3)

where \( X_f \) is the volume fraction of the nanoparticles, \( x_1 \) is the thickness of the nanoparticles, \( Y_1 \) is the thickness of the host polymer, and \( T_{tot} \) is the total thickness of the film. These formulae assume perfectly spherical particles, uniform packing with a maximum packing density of 75% (the actual maximum packing density of spheres is a little over 74%), and all void space between particles filled in completely with host polymer with no air bubbles. The higher volume fraction of nanoparticles proved to have significantly higher dielectric values in most cases, and was solely used during any further measurements or comparisons.
There was a small possibility that the ligands might semi-helicize (it takes a 14 carbon chain to form a single half-helix, while none of the ligands was that long and the shortest ligands would have greater likelihood of adopting an anti-conformation rather than gauche), and in doing so potentially provide complex forms of interaction between neighboring nanoparticles. To confirm that this was not the case, the dielectric spectra of three different chain-length ligands are directly compared in Figure 5. As can be observed, differences in chain length lead to negligible changes in dielectric properties. From this can be concluded that the length of the ligand is not responsible for the observed dielectric properties. The lack of interaction likely means that longer ligands formed into a gauche semi-helix, blocking the carbon chain from interacting with its environment, while the shortest of ligands did the same, were too short to reach more than a few neighboring ligands, or that even if the interactions did occur, length had no effect on the dielectric properties.

Figure 3.2. Effective dielectric constant and dielectric loss of ligand functionalized nanoparticles with differing reactive heads compared. Between 100 Hz and 2 MHz, the dielectric values of BST shows a 56% decrease, 5PF-A a 38% decrease, 5PF-CA a 19% decrease, and 2PF-PA a 33%.
Being now able to discard the effects of the differing chain lengths meant that it was now possible to directly compare three different ligands based upon their reactive heads (since the chain lengths are slightly different). In examining Figure 3.2, significant differences in dielectric properties between the ligands may be observed. While amine-terminated PFPA shows itself to have the highest dielectric constant, it also exhibits the <1kHz dielectric constant drop characteristic of surface water adsorption, as well as having the highest dissipation value of the ligand-reacted samples at low frequencies.

Similarly, phosphonic acid-terminated PFEPA also shows a large decrease in dielectric constant over the frequency range and the second-largest low frequency dissipation value. In contrast, carboxylic acid-terminated PFpentA shows a lower dielectric constant, but it is extremely stable over the entire frequency range, as well as having a dissipation value nearly half that of the other samples.

From this data, it can be concluded that either the ligands are attaching to the hydroxyl groups on the surface of the nanoparticle and forcing the water molecules away from the surface...
of the nanoparticle, or the ligands are acting as single-molecule moisture scourers, and simply doing a good, but semi-temporary job of removing the adsorbed moisture. Semi-temporary because in this case, the nanoparticles would be encased in the PFA polymer and protected from environmental moisture.

3.2. Fourier Transform Infrared Spectroscopy and Thermogravimetric Analysis

While the Fourier Transform Infrared Spectra (FTIRs) for most of the samples show only small amounts of ligand attached, BST-2PF-PA, the phosphonic-terminated ligand, proves to be the sole example of a sample which shows strong, distinct CF2 and CF3 peaks with signals in the 1000-1250 wavenumber range. While other samples seem to indicate some smaller amounts still attached (notably BST-7PF-CA), BST-2PF-PA proves to have been the most effective at keeping the ligand attached, a detail significant for future consideration of longer-term stability. While a lack of visible peaks at 1000-1250 wavenumbers does not mean that no ligands are present, it does mean that the concentration is very low, and that the method is viable for use in systematic identification of presence of higher concentrations of ligand.
Figure 3.4. FTIR of barium strontium titanate nanoparticles and associated ligand-functionalized variants. Spectra offset vertically for clarity. C-F$_2$ and C-F$_3$ peaks only clearly visible with BST-2PF-PA and BST-7PF-CA. Of note, BST-5PF-A and BST-7PF-A, both of which were incapable of forming thin films, also show no C-F$_2$ or C-F$_3$ peaks.
Figure 3.5 Thermogravimetric analysis of ligand-functionalized BST nanoparticles. Derivatives for carboxylic nanoparticles artificially separated for clarity. All samples oven dried in a 100 °C oven. overnight, then sealed before measuring.
Dry mass % = \frac{(100 - T_1 Wt \%) - (100 - T_0 Wt %)}{(100 - T_0 Wt %)} \quad (3.4)

Reduction in water % = \left[ 1 - \left( \frac{\text{Dry mass } %}{\text{BST dry mass } %} \right) \right] \times 100 \quad (3.5)

Dry mass % is usually used to re-assign a new maximum mass % in thermogravimetric analysis (TGA) after all atmospheric water has been burned off. However, since our interest lies in evaluating the amount of hydroxyl groups found on the surface of the nanoparticles, the temperature range that it covers is also shifted. Though the samples were dried in an oven overnight, an unknown amount of moisture was nonetheless absorbed during various transfer processes. This adds an unknown, but judging from the TGA curves, minor inaccuracy to any performed calculations below ~300 °C. Nonetheless, it does show how much mass % was lost using the newly adjusted scale. This in turn allows the use of Equation 3.5 which compares the amount of surface adsorbed water between the ligand functionalized nanoparticles and the unmodified nanoparticles. The results of Equation 3.5 may be seen in Table 3.1.
Thermogravimetric analysis reveals a somewhat different story than FTIR. All samples show a decrease in surface adsorbed water molecules, with efficiency following the trends PA>CA>A.

<table>
<thead>
<tr>
<th></th>
<th>3PF-CA</th>
<th>5PF-CA</th>
<th>7PF-CA</th>
<th>3PF-A</th>
<th>5PF-A</th>
<th>7PF-A</th>
<th>2PF-PA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt % lost from ligand</td>
<td>0.7</td>
<td>0.7</td>
<td>0.8</td>
<td>0.6</td>
<td>0.4</td>
<td>0.8</td>
<td>1.1</td>
</tr>
<tr>
<td># ligands in sample</td>
<td>4.6 x 10^{20}</td>
<td>6.32 x 10^{19}</td>
<td>9.28 x 10^{18}</td>
<td>7.94 x 10^{19}</td>
<td>2.94 x 10^{19}</td>
<td>2.88 x 10^{19}</td>
<td>1.71 x 10^{20}</td>
</tr>
<tr>
<td># NP in sample</td>
<td>3.80 x 10^{17}</td>
<td>1.07 x 10^{17}</td>
<td>1.70 x 10^{16}</td>
<td>8.85 x 10^{16}</td>
<td>8.23 x 10^{16}</td>
<td>5.55 x 10^{16}</td>
<td>1.38 x 10^{17}</td>
</tr>
<tr>
<td>ligands per NP</td>
<td>1.21 x 10^{03}</td>
<td>5.93 x 10^{02}</td>
<td>5.45 x 10^{02}</td>
<td>8.97 x 10^{02}</td>
<td>3.57 x 10^{02}</td>
<td>5.19 x 10^{02}</td>
<td>1.24 x 10^{03}</td>
</tr>
<tr>
<td>%OH reacted</td>
<td>4.84%</td>
<td>2.37%</td>
<td>2.18%</td>
<td>3.59%</td>
<td>1.43%</td>
<td>2.08%</td>
<td>4.96%</td>
</tr>
</tbody>
</table>

Table 3.2. Amount of surface hydroxyl groups reacted with by each ligand. Values taken from TGA data.

Several distinct peaks are visible in the derivative spectra for each sample. 90-95 °C degrees represent any moisture left over in the sample. At ~160 °C, surface adsorbed water begins to remove from the surface. There are two peaks which are difficult to resolve, ~280 °C and ~320 °C. The 280 °C represents the removal of the attached surface ligands, while the 320 °C likely represents a trace impurity of a small amount of isopropoxide remaining attached to the surface titanium groups as a vestige of the nanoparticle synthesis. 370 °C represents the removal of surface hydroxyl groups. Finally, at ~470 °C is the removal of lattice hydroxyl ions, vestiges of the solvothermal synthesis.
The 280/320 °C peaks are expected, as the ligands are attached to the surface hydroxyl groups, and so any left attached to the nanoparticle would be removed as the surface hydroxyl groups are removed. The noise in the amine ligand derivative seems to stem from the two peaks overlapping to present as a single peak. All calculations taken from measurements at 280, 370 °C degrees.

Examining the 370 °C peaks reveals a curious anomaly. Carboxylic acid terminated ligands show equal mass % reduction at both 280 °C and 370 °C. In contrast, amine-terminated ligands show a steadily increasing reduction in mass % as the ligand grows in length. Finally, the phosphonic acid terminated ligand shows the largest decrease in mass %. These changes indicate somewhat more complex interactions at the ligand-nanoparticle interface.

Using the valued obtained from TGA allows calculation of the degree of surface hydroxyl functionalization (see Table 3.2). Though the functionalization is not large, it does reveal a few trends. I hypothesize that this coverage behavior may be explained by the dentation of the reactive head. Carboxylic acid would be expected to only form a monodentate attachment—that is, react with only a single surface hydroxyl group. Having an equal drop in mass percent from both the ligand contribution (at 280 °C) and from the surface hydroxyl group (at 380 °C) indicates that a uniform removal in a 1:1 ratio of ligand:surface hydroxyl group has been achieved.

When we examine the phosphonic acid head, we see a 136% decrease in mass percent between 280 °C and 370 °C. If the phosphonic acid were to be fully bi- or tri-dentate (assuming that in doing so, all attached hydroxyl groups would be removed upon reaching 280 °C), we would expect to see a reduction of 200% or 300%, respectively. Instead, this indicates that there
is a mixture of differently dentated ligands attached to the surface. This is to be expected—dentation and monolayer density between phosphonic acid and metal oxides is highly influenced by the presence of water, which is known to be on and around the surface of the nanoparticle. Determining the degree of dentation and the relative ratio of each would require further study. As an educated guess, however—tridentate phosphonic acid attached to metal oxides tends to only be observed in experiments where water is completely excluded, while increased presence of water does lend itself to bi-dentate forms as well as neighboring phosphonic acidsed to one another. If we therefore assume that the number of tridentate phosphonic acid ligands present is negligible, then roughly 1/3rd of the phosphonic acid ligand attached to the surface of the nanoparticle had the necessary localized environment (water presence, high local density of surface hydroxyl groups to attach to) to assume a bidentate form. This in turn strengthens the hypothesis regarding interactions of the PTFE tails of the ligands, as at least 1/3rd of the surface hydroxyl groups are in neighboring proximity.

The most curious of the observed changes in mass percentage comes from the amine terminated ligands. As a reminder, the 3- and 7- carbon backbone ligands were unable to be formed into thin films capable of producing a readable capacitor, but showed usually high viscosity upon mixing with PVP. The 5 carbon backbone, however, was able to form a film, and shows the expected 1:1 ratio of ligand:hydroxyl group removal. One possible explanation for this observation may be that the samples were heated too rapidly, which resulted in an artificial reduction of the mass percentage over the measured temperature range. This could also explain why the three ligands do not follow a longer-to shorter or shorter-to-longer pattern of efficiency. Another explanation comes from the attempt to use the amine-terminated ligands for filmmaking properties. On doing so, the 3PF-A and 7PF-A both formed a gel-like consistency, which
prevented them from being able to be effectively spin-coated. This can indicate a much higher density of ligands on the surface of the nanoparticle, as well as more unbound ligands which were loosely associated with the nanoparticles. Examining Table 3.1, 3.2 and the TGA data, 3PF-A and 7PF-A both show having greater amounts of ligand present, as well as being more effective at removing water than 5PF-A. Why 5PF-A did not show this trend is unclear. However, as the amine-terminated ligands proved to be inferior to both other types of ligands (in terms of poorest loss characteristics, film-making properties, surface attachment) as expected, further time spent studying the matter to determine an exact solution for the problem was deemed moot.

The data initially appears to lead to some conflicting conclusions and further investigation was merited. For example, the phosphonic-acid terminated ligand shows itself to have the greatest adhesion to the surface of the nanoparticle. In which case, why does the TGA seem to show it as having a larger amount of water loss than other samples? We hypothesize the explanation as follows: the surface-adsorbed water is removed during the surface functionalization process. However, either the water just removed, or water formed as a byproduct of the surface functionalization, is hydrogen bonded to the acid reactive head. It is far enough away to no longer influence the nanocrystal, but still trapped within the confines of the PTFE ligand tail. Because of this, the water is only driven off at higher temperatures, which creates the drop in weight of the sample. One possible way to test this hypothesis would be to heat the sample to 120 degrees C until weight change is no longer observed. This would serve to remove atmospheric water as well as surface adsorbed water. However, doing so to the BST would also drive off some of its surface adsorbed water, making the direct comparison between the two incorrect.
3.3 Scanning Electron Microscopy and Film Quality

To examine the changes to the film-making properties after surface functionalization, a series of films of different thicknesses was prepared. Scanning electron micrographs (SEMs) show no particular change in NP shape, still being roughly spherical, with a diameter of ~25 nm.

Figure 3.6. Comparison of film making properties of pure unmodified BST nanoparticles (left) versus pure functionalized BST nanoparticles (right).

Figure 3.7. Side view of ligand-modified nanoparticle film suspended in PVP polymer, ~2 µm thick.
Figure 3.8. Top: Pure BST-5PF-A nanoparticle film in surface-conjugated rich area. Other ligands showed similar areas of high ligand density. Bottom: Pure BST film.
The most dramatic difference may be observed in the thinnest films (Figure 3.6), which were only 2-3 layers of nanoparticles thick. The ligand functionalized nanoparticles show dramatically improved thin-film formation, while regular BST forms thickened islands of material. When a film is viewed from the side (Figure 3.8), it also clearly shows a high quality film with no major voids or holes, with a low surface roughness.

SEMs of just the nanoparticles were taken to compare the quality of the films forms before and after surface conjugation, but without the suspending polymer matrix (Figure 3.6, 3.8). The surface conjugated nanoparticle samples showed areas where the ligand density was very high, and other areas where it was entirely absent. This indicates two important points: 1. the method of separating conjugated and non-conjugated nanoparticles (separating those nanoparticles which are suspended in solution, and those which have precipitated out of solution) needs to be further evaluated. One solution would be to use fluorinated solvents, which would allow only the nanoparticles with a high ligand density to remain suspended in solution. 2. Measurements of surface functionalized nanoparticles are all tainted to a degree with unmodified nanoparticles. For example, in the FTIR spectra, the strong -O-H peaks can much more easily mask the N-H peaks found in the amine terminated ligands. TGA will also show a greater water and surface hydroxyl loss than would be observed with samples which are fully surface functionalized. The dielectric spectroscopy measurements will also show characteristics of water adsorption where fully surface-functionalized nanoparticles would not. However, when examining the dielectric spectroscopy of the nanoparticles, the effects of water adsorption are strongly muted, which indicates that samples are still mostly made up of functionalized particles.
Chapter 4
Conclusion

This study set out to explore the effect of several commercially available compounds used of ligands on dielectric $\text{Ba}_{0.7}\text{(Sr}_{0.3}\text{)}\text{TiO}_3$ (BST) nanoparticles, and has identified the degree of surface functionalization, the changes in film-making properties, and the changes in dielectric properties of resultant films. The study sought to answer the following questions:

1. Does the reactive head of the ligand affect the degree of surface functionalization?

2. Does a teflon-like ligand tail allow complex 3D interaction between the nanoparticles?

3. Does the length of the ligand tail affect interactions between nanoparticles?

4. Do the ligands effectively remove surface adsorbed water from the nanoparticles?

5. Do any of these changes affect the dielectric properties (effective dielectric constant, dielectric loss) of a thin film capacitor made from the nanoparticles?

Dielectric BST nanoparticles were synthesized using the standard solvolysis method, then refluxed in the presence of the ligands. The samples were then analyzed, and suspensions of them in PVP polymer were spincoated to form thin film capacitors, the dielectric spectra of which were correlated with the nanoparticle analyses. In doing so, answers to these questions were made available.

Q1. Does the reactive head of the ligand affect the degree of surface functionalization?

A1. Yes. The study had hypothesized that the phosphonic acid terminated ligand would show the greatest degree of surface functionalization, followed by carboxylic acid, and finally by
the amine terminated ligand. The phosphonic acid and carboxylic acid were hypothesized to be able to form some bidentate forms, and have some stabilization from neighboring hydrogen bonding. Amine, on the other hand, would hydrogen bond with surface hydroxyl groups and with vacant surface titanium ions.

Q2. Does a teflon-like ligand tail allow complex 3D interaction between the nanoparticles?

A2. Yes and no. SEM seems to indicate that in areas of high ligand density, the ligand does effectively fill the interstitial spaces between nanoparticles. Rather than the teflon ligand body forming a crystallized structure, instead an amorphous structure appears to form. This random orientation can, in turn, lead to more robust, flexible thin film capacitors.

Q3. Does the length of the ligand tail affect interactions between nanoparticles?

A3. No. Data indicates that the length of the ligand did not affect interparticle crystallization in any way. Instead, the length of the tail affected the amount of surface adsorbed water released from the sample into the suspending solvent.

Q4. Do the ligands effectively remove surface adsorbed water from the nanoparticles?

A4. Yes. Surface functionalization showed up to a 27% reduction in surface adsorbed water.

Q5. Do any of these changes affect the dielectric properties (effective dielectric constant, dielectric loss) of a thin film capacitor made from the nanoparticles?

A5. Yes. Reduction of surface adsorbed water was visible in the dielectric spectra of the resultant thin films. Samples which had more water removed proved to have flatter, more stable
effective dielectric constants across the measured frequency range. In addition, the amount of surface adsorbed water removed correlates with a reduction of dielectric loss- the more water which was removed, the lower and flatter the dielectric loss was.

There were several possible explanations for this. The fluorinated part of the ligand could act as an electron withdrawing group, enhancing the dipole of the unit cell of the surface of the nanoparticle. But the ligands had a cancelled out dipole due to the helicization, and if this were the case, longer ligands would have shown a stronger effect.

Another explanation was that the reactive heads removed water and prevented more from being adsorbed onto the surface, improving the dielectric properties. But while the change in dielectric loss and the stability of the dielectric constant do show a correlation with the removal of water, this does not explain the consistent reduction in the dielectric constant.

When BST is made in nanoparticle form, there is a subsequent lowering of the Curie temperature. With nanoparticle sizes such as used in this study (~25 nm diameter), the Curie temperature will be slightly above room temperature. The solvothermal synthesis produces uniformly cubic nanoparticles with a degree of tetragonal character. While the amine ligand coordinated with surface titanium ions, both carboxylic and phosphonic ligands were capable of reacting with surface hydroxyl groups, as well as forming bidentate dorms with the carbonyl or phosphoryl oxygen coordinating with nearby titanium ions, or H-bonding with neighboring ligands. The action of doing so reduced the internal strains of the surface unit cells, which removed some of the tetragonal character, making them slightly more cubic- which in turn decreased the dielectric constant. Since the degree of surface functionalization is not high, a large, dramatic decrease in dielectric constant would not be expected- and indeed, this is exactly
what is observed. It is noteworthy that the phosphonic acid ligand shows both the greatest surface coverage, as well as the lowest dielectric constant. The amine would be expected to be less effective because it isn't reacting with the surface, only associating with it. Carboxylic acid both doesn't over-react with the surface, and is the most successful at removing water. This shows a decreased dielectric constant (though not as decreased as the phosphonic acid ligand), as well as the lowest dielectric loss of any of the samples.

With regards to the changes in dielectric loss, this can be explained as the removal of surface adsorbed water from the nanoparticle. The carboxylic acid was best at removing water, and has the lowest dielectric loss. The phosphonic acid and the amine were roughly equal at water removal and both have roughly the same dielectric loss. When looking at the change in dielectric value over the frequency range, the changes are almost the same as well (38% for carboxylic and 33% for phosphonic). The amine removed slightly less water, has a slightly higher dielectric decrease over the frequency range, while having a slightly higher dielectric loss than the phosphonic acid.

In future studies, surface hydroxylation proved unnecessary to provide significant changes to the nanoparticle properties. However, further functionalization would be worthwhile to assess the effect of increased loading. In addition, the ligand may be changed to take a more active role in the dielectric constant of the nanoparticle thin film. An example would be a PVDF-type ligand.

In addition, better methodology must be developed to separate surface-modified nanoparticles from non- or under-modified nanoparticles. As suggested in the text, one method may be to suspend the particles in a fluorinated solvent to enhance the separation.
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Appendix A

Fabrication and Testing of Capacitor Devices.

Of equal importance as the synthesis of the dielectric material is the fabrication of the capacitor device itself. Manufacture of nanoparticle-based capacitor devices requires attention be paid to a number of seemingly minor features. These features include surface roughness of both electrode and dielectric film, consistent thickness of the dielectric film, hole-free films, resistance of the electrodes, the layout, and method of measurement. These details must be considered when manufacturing capacitor devices, otherwise it is effectively impossible to successfully manufacture capacitors both in high numbers and with consistent capacitance properties.

This chapter will be broken into the following sections:

A1.1 Electrode formation

A1.2 Thin film formation of nanoparticle dielectric

A1.3 Dielectric spectroscopy of capacitors.

A.1 Electrode Formation

Parallel plate thin film capacitors have a number of stringent requirements to ensure optimal performance.\(^1\)\(^-\)\(^12\) In this section will be discussed the manufacturing requirements of a metal thin film electrode used in the capacitors, and how those requirements were ultimately met.
A.1.1 Sputtering Electrodes

Our manufacturing process uses metal electrodes for the top and bottom plates of the capacitor. Initial experiments used a Denton benchtop sputter coater to sputter gold onto glass substrates. Sputter coating works by bombarding a metal source with high energy argon plasma to knock atoms off of the target and spray the substrate, creating a thin film of the target material on the substrate. One of the major advantages of this technique is that it allows thin films of high melting point compounds to be made much more quickly and at lower temperatures than in thermal-type evaporators. It is also able to provide repeatable film thicknesses from sample to sample, and turnaround time is low.

On closer examination of our samples, however, we discovered a number of drawbacks to sputter coating. Our sputter coater had difficulty maintaining repeatable thickness from sample to sample. While thicker electrodes would have solved this, the aim was to have electrodes with a thickness of \( \sim 50 \text{ nm} \) due to the design of the capacitors. We found too that the surface roughness of the resultant film was too high for our samples, due to the large resultant grain sizes of the gold. As mentioned before, the surface roughness is critical for electrodes. Finally, we found that sputter coating lead to a much larger number of non-functional capacitors when compared to electrodes which were thermally evaporated. This could have been due to a combination of the high energy deposition and the large surface roughness. The solution proved to be designing a thermal evaporator.
A.1.2 Thermal Evaporation

A thermal evaporator at its most basic operates by thermally melting a material under vacuum and bringing the material to the boiling point where evaporated material is deposited onto the substrate. In practice, we use a tungsten boat to hold the metal to be evaporated, generally gold, silver, or chromium. The tungsten boat is placed between a pair of electrodes within a bell jar. The bell jar is pumped down to an atmosphere of $10^{-5}$ Torr. At this point, a current is run through the boat. As with an old-fashioned tungsten filament light bulb, the tungsten boat quickly heats under the applied current. The reduced atmospheric pressure depresses the boiling point of the metal. The current is adjusted until the desired rate of deposition occurs, with a feedback loop through the thickness monitors placed between the boat and the rotating sample stage.

While it may seem obvious to crank the current up, increasing the deposition rate, in practice, the opposite proved to be more desirable. A higher current, and therefore a hotter boat, results in a more violently boiling metal, which leads to inhomogeneous deposition of the metal on the substrate. Instead, a lower, slower rate of deposition is usually preferred- generally heating the metal to just at the boiling point, or even slightly below, encouraging a rapid and more uniform vaporization of the metal onto the substrate. Note that this concern is valid when
making very thin films (<50 nm). When making films of metal which are sufficiently thick (hundreds of nm) a higher current can usually be used as the Inhomogeneities mostly cancel out over time.

When making a thin film capacitor, care and attention must be paid to the electrode plates used to sandwich the dielectric film. The material must be capable of forming a low-roughness interface between the electrode and the dielectric. It must also have a sufficiently low, and known resistance which can be taken into account for calculations on efficiencies of the overall capacitor, as they can add a significant contribution to the overall ESR. In our experiments, gold is commonly used for the interfacial layer, with chromium as an adhesion layer.

Gold and silver, while both excellent electrode materials, have a tendency to not adhere well to glass or silicon, resulting in measurement problems later when determining the capacitance of the capacitor; the probes have a habit of scraping off the bottom electrode and not making good contact as a result. The solution was to use chromium as an adhesion layer. Though its toxic qualities are well known, it is an inexpensive material which functions well as an adhesion layer, although due to chromium sublimating rather than boiling, care is necessary when setting up the evaporation. Our thermal evaporator was of necessity a dual-source system. After evaporating the chromium adhesion layer, the next layer must be evaporated on before the substrate is exposed to the atmosphere. Between dust and a thin chromium oxide layer forming, the next layer would be prevented from properly adhering to the chromium layer.

A.1.3 Probe Considerations

When measuring a thin film capacitor, several considerations must be made to ensure the highest accuracy in measurement.\textsuperscript{13-20} The frequency range dictates the types of probes which
may be used, which in turn dictates to an extent the form factor of the thin film capacitor. When capacitance measurements were first begun, an Agilent 4284A LCR meter capable of reading up to 1 MHz was available. At these low frequencies, test measurement requirements are much less stringent. However, upon purchase of a more modern set of instruments, an Agilent 4294A LCR meter and an Agilent E4991A impedance analyzer, extending the measurable frequencies into the lower RF (3 GHz), attention to the test measurement requirements became absolutely critical. This required both careful selection of a specific probe type and a radical redesign of the thin film capacitors.

The top and bottom electrodes must be the same height. The probes are manufactured to be the same height because the probe is normally held stationary and the sample is raised up to it. The reason for this is because moving the probe changes the calibrated distances. However, our probe station setup does not have a z-adjustable stage. To make up for this, the probe itself was designed with a semi-rigid cable attached along the micromanipulator which would tilt towards the substrate, minimizing the change in the cable. However, the probe tips are nonetheless the same height. In order for one tip to penetrate the film and hit the bottom electrode, the top one will also pierce through both the top electrode and the bottom one. And while the micromanipulator does allow the angling of the probe tips, the angle would be so slight, a fraction of a degree, that it would be impossible to adjust it so from sample to sample accurately.

The electrodes can be a certain maximum distance from one another. This distance changes depending on the frequency. If a GS or SG probe is used, the recommended distance between the ground pads is $0.02\lambda$ which at 3GHz is 2 mm. If instead a GSG style probe is used, that distance is $0.05\lambda$ which is 5mm. This is due to the transition of the electric field pattern from
the coaxial cable to the probe tip with a different (flatter) electrical field pattern. Higher quality signal (and more accurate results at frequencies above 3 GHz) is achieved by having the greatest quality transition between these two patterns.

When using a GSG probe, a short, symmetrical electrical field between G and S is produced. When GS or SG is used, the field is longer and asymmetrical, as can be seen in Figure A.3. This also forces the requirement of the electrodes being parallel to one another. As seen in Figure A.3, this was not originally the case. In effect, the electrical path length between G and S
is different, and effectively becomes a form of inductance. SG/GS probes have about four times as much of this inductance as GSG, and there is a corresponding reduction in the useable bandwidth. This only gets worse with larger pitches and higher frequencies. At lower frequencies, however, the correction for this allows the GS probe to have greater accuracy than GSG.

In order to function correctly, the probe would need to rest atop the thin layer of gold of the top electrode, but instead, the probe would often punch through the delicate top layer. The GS probe used is calibrated assuming air between the two probes. Having one probe sink into the dielectric film understandably changes the electrical properties of the space between the two probes, which in turn throws off measurement accuracy. To address this issue, a new mask design was created which allowed the researcher to touch the probes to the capacitor without worry of puncturing into the dielectric film (Fig A.3).

**A.1.4 Parallel Plate Manufacturing Requirements**

**A.1.4.1. Surface Inhomogeneities**

The capacitance of a parallel plate capacitor derives from the thickness of the dielectric film at its most narrow point. For example, if a manufacturing process leads to a projection of the electrode material into the dielectric film, the capacitance is determined as the result of the thickness of the dielectric between the tip of the projection and the opposing electrode. The cause of this is the percolation of electrons through the capacitor; the shorter distance between electrodes, the increased likelihood of electrons percolating through the dielectric from one electrode to the other. Indeed, at sufficient thinness, electrons will begin to tunnel between electrodes, the mechanism behind metal-insulator-metal devices.\(^{1-12}\)
The lowered resistance (again, due to the decreased distance) will mean that the energy barrier to electrons will be lower in this localized area, and more will go through. Using the classical water analogy, a pair of parallel pipes of equal size will transport the same amount of water. When one pipe is larger, however, more water will flow through it than the thinner pipe, showing that lower resistance pathways will tend to have increased amounts of current flowing through.

This sort of manufactured flaw can quickly lead to more than just a decrease in the overall capacitance of the capacitor. It may also result in the electrode acting as something of a lightening rod- concentrating the stream of current onto a tight point, heating and melting the electrode there, while thermally damaging the surrounding dielectric. In some cases, it can lead to a cycle of melting and solidifying of the flaw and eventually turn into a dendritic structure, working its way over time to the opposite electrode, ultimately shorting the capacitor.

While this example discusses only a single irregularity in the surface of the electrode, a high surface roughness leads to the same sort of changes over the entire area of the capacitor, decreasing the overall capacitance. For this reason, it is important to examine manufacturing methods which demonstrate the ability to form minimal surface roughness metallic films.

A.1.4.2. Resistance of Electrodes

The resistance of a material is highly geometry dependant- a shorter, fatter wire has lower resistance than a longer skinnier wire. Again using the classic water analogy, more water can pass through a wider pipe than a narrower pipe. This can be seen when calculating the resistance of the electrode.
\[ R = r \frac{A}{l} \] (A.1)

where \( R \) is the resistance of the electrode, \( r \) is the resistivity of the material, \( A \) is the cross-section area of the electrode, and \( l \) is the length of the electrode. In practice, when dropping the resistance, it is easier to increase the thickness of the electrode than to change the pathlength of the electrode (requiring a constant re-design of the capacitor). This is one of the reasons for the robust utility of MLCCs, where square area on a circuit board is a premium, but height is less so. Table A.4 shows an example of some calculations which demonstrate the linear relationship between the thickness of the electrode and the resistance.

### A.2.0 Thin Film Formation of Nanoparticle Dielectric

There are two ways to create a thin film: the top-down and the bottom-up approach. The top-down approach is to grind bulk material down and sinter it into a thin film. The top-down approach tends to be more difficult and more expensive. The cost of both the machinery and the reagents involved is prohibitive. The thickness of the eventual film is fundamentally limited by the mechanical processes used to create the thin films. Top-down does not allow the fine control of the crystalline structure of the film itself.

The bottom-up approach is to grow the film on the substrate itself, whether through molecular beam epitaxy, spin-coating, or atomic force microscopy. Spin-coating has the advantage of being both bench-top accessible and inexpensive, while retaining control over the alignment of the nanoparticles in the resultant film. Colloidal deposition rarely requires high temperatures, expensive reagents, or unusually expensive equipment. Colloidal deposition allows

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Resistance (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.488</td>
</tr>
<tr>
<td>75</td>
<td>0.325</td>
</tr>
<tr>
<td>100</td>
<td>0.244</td>
</tr>
<tr>
<td>150</td>
<td>0.163</td>
</tr>
</tbody>
</table>

Table A.1. Example resistances of gold electrodes, assuming 1 mm² area.
the researcher to create hole-free nanoparticle films with different properties merely by changing some of the chemical conditions (solvent, temperature) of the colloidal solution.

There are several problems with the barium strontium titanate nanoparticles under study. They do not stay suspended in solution for very long. They also have a tendency to agglomerate very quickly, even following intense sonication. The solvents within which the nanoparticles can be suspended are limited. There is also concern about the amount of free space between the particles in films. These problems can all contribute to poorly formed films, and lossy, leaky capacitors.

A.2.1 Sonication

BST nanoparticles have a tendency to form aggregates in solution. These aggregates, measuring from tens of nanometers to a micron in diameter, are likely due to surface interactions between the surface hydroxyl groups forming hydrogen bonds between the particles, though this has not been investigated.

Aggregates present a twofold problem. First, the structure of the aggregate prevents interpenetration of the host polymer from breeching the internal nanoparticles. This leaves large amounts of air in the space between the particles, areas where the dielectric value of the film drops significantly. Too, once under load, the aggregates, possible due to the air between the particles, have been seen to erupt with enough force to pierce the upper electrode and destroy the capacitor. Since the aggregates form while in ethanol solution, the interstitial spacing likely has a fair amount of ethanol present, which could vigorously expand under an applied electrical field.
Equally important, the aggregates can often be found on the surface of the thin film. Our goal thin film thickness is ~250 nm; dropping an aggregate atop of a film of this thickness disrupts the surface roughness homogeneity to an extreme level, especially in the cases where the aggregate may be larger in diameter than the film is thick.

To address the aggregates, it was found that a sample could be sonicated with a sonication wand for a short period of time in order to break the aggregates up. Doing so would grant an aggregate-free solution for upwards of a day before the aggregates would again begin to form.

A.2.2 Spin Coating

There are a number of different methods, such as ink jet and injection printing, by which the dielectric film can be manufactured. For small-scale manufacture in a laboratory setting, we chose to go with spin coating as the best compromise of cost, ease of use, repeatability, and reliability.

Spin coating involves holding the substrate with the bottom electrode in place on a turntable with vacuum. The turntable is then spun upwards of tens of thousands of RPM. In doing so, liquid samples are repeatably flattened to known thicknesses with excess flung off of the edges. Spin coating does have the drawback that the film thickness is generally slightly thicker in the center of the turntable, as well as on the very edge of the sample (if it has not been flung off the edge). Needless to say, an inhomogenous sample when spin coated will result in large tears and streaks in the formed thin film, potentially to the point where the film cannot be used.
Nonetheless, BST is able to be consistently synthesized in a well-distributed manner, particularly following sonication. When an aliquot at known concentration is dropped onto the substrate in the spin coater, it can be relied on to form consistent thickness thin films.

In materials science, percolation theory concerns itself with the probability that the path of the electron through a dielectric medium can pass from one electrode to another without being intercepted by the dielectric medium. This encompasses a number of concerns; sample roughness, choice of metal for electrodes, packing density of the nanoparticles, and thickness. There is a minimum thickness of nanoparticles required to prevent electrons from percolating from one electrode to the other. This is not an average calculation, but rather is determined by the thickness at the thinnest point of the dielectric material. Because of this, surface roughness can intensely affect the capacitor, as peaks in the electrode can match with valleys in the dielectric.

In an ideal film, the roughness RMS will approach that of the radius of the nanoparticle. Depending on the film created, this can be approached. This issue may also be addressed by coating the nanoparticles with a polymer to infiltrate the nanoparticles before plating the top layer of metal, but this can lead to complications arising from the multiple-interface nature of the setup. The concern with roughness also affects the choice of metal for the electrodes. All metals will form dendrites under an applied voltage; the question is more one of extent of dendrite formation. The greater the extent of the dendrites, the thinner is the film at the thickest point, and this can easily lead to shorting as the two dendrites meet one another within the dielectric.
A.3.0 Dielectric Spectroscopy of Capacitors

A.3.1 Ohm’s Law

To understand how dielectric spectroscopy works requires an understanding Ohm’s Law and impedance.\textsuperscript{21-45}

Ohm’s Law describes the relationship between voltage (V), current (I), and resistance (R) as follows:

\[ I = \frac{V}{R} \quad (A.2) \]

Or, the current through a component is equal to the voltage applied across the component divided by the resistance of the component. This most basic version of Ohm’s Law is only valid in a DC circuit. When AC or time-varying voltage/current is applied, the relationship between voltage and current becomes the solution of a differential equation. The basic form of Ohm’s Law does
not directly apply, since it only contains resistances of value R, rather than the complex impedances which may be present. The general form of Ohm’s Law still applies, however, with complex scalars taking the place of the voltage and current, and the complex impedance (Z) taking the place of resistance, though impedance retains the same units as resistance (Ohms, Ω).

\[ Z = \frac{V}{I} \] (A.3)

### A.3.2 Impedance

Impedance has two components: the real component, Resistance (R), and the imaginary component Reactance (X). This relationship is described as follows:

\[ Z = R + jX \] (A.4)

Here, \( j \) is the imaginary constant and replaces the more usual \( i \) to prevent confusion with the symbol for current (I).

There are two forms of reactance, inductive \((X_L)\) and capacitive \((X_C)\). For the purposes under investigation here, we need only concern ourselves with capacitive reactance. Capacitive reactance may be defined as:

\[ X_C = \frac{1}{2\pi f C} \] (A.5)

Where C is capacitance, and \( f \) is the frequency of interest. For easier notation, \( 2\pi f \) is usually replaced by the angular frequency \((\omega)\), becoming:

\[ X_C = \frac{1}{\omega C} \] (A.6)
The Dissipation Factor (DF) is an indicator of the energy efficiency of a capacitor; that is, how dominant the resistance is versus the reactance. It is defined as the ratio of energy dissipated in a component to the energy stored, or:

\[ DF = \frac{R}{X} \] (A.7)

DF may also be expressed at the tangent of the angle \( \delta \) from figure 2.5, which is why it is also commonly referred to as simply the tan delta.

Impedance can be expressed in either rectangular coordinate form as \( R + jX \) or in polar form as \( |Z| \angle \theta \), indicating the magnitude and phase angle.

\[ Z = R + jX = |Z| \angle \theta \] (A.8)

At low frequencies, the phase angle (\( \theta \)) is \( \sim -90^\circ \) so the reactance is capacitive. The capacitor frequency response reaches a minimum impedance point at a self-resonant frequency, after which the capacitor acts as an inductor rather than a capacitor. At the self resonant frequency, the capacitive and inductive reactance values are equal. As a result, the phase angle is \( 0^\circ \) and the capacitor is resistive. When the frequency is raised above the self-resonant frequency, the phase angle changes to \( +90^\circ \) which shows that the inductive reactance (parasitic inductance) has become dominant.
A.3.3 Auto-Balancing Bridge Measurement Method

When calculating the impedance, two separate quantities must be measured in order to calculate the impedance, due to the complex nature of impedance. However, impedance analyzers operate by using a standard ranged resistor to calculate one of those values, and measure the change in voltage across the capacitor to calculate the other. It is still important to note that in an AC field, voltage is also a complex quantity, so simply measuring the change in voltage across a capacitor is not sufficient to calculate the impedance.

In an auto-balancing bridge (ABB, figure A.6), the bridge is said to be balanced when its detector measures a mean current or voltage of zero. This condition is attained by injecting a corresponding voltage/current. Each of these injections is matched to the incoming current/voltage in terms of the phase and quantity due to the detectors in the circuit. The ABB is distinguished from a balancing bridge circuit by having this injection matching done automatically by the system rather than by a skilled operator.

The obvious question is why the instrument doesn't simply read the signal coming straight out of the DUT. This is because the ABB enhances (amplifies and reduces noise) the signal, giving much greater accuracy.

The ABB measurement method requires the instrument to know the voltage applied to the DUT, and the current flowing over the DUT. The test signal current (Ix) flowing through the DUT also flows into the I-V converter. Within the negative feedback loop, the operational filter of the I-V converter makes the same current as Ix flow through the range resistor (Rr).
A range resistor is a built-in variable resistor of known resistance at the set frequency. When the current (called the feedback current, $I_r$) flowing through the range resistor $R_r$ is different from the current flowing through the DUT ($I_x$), an imbalance current ($I_x - I_r$) flows into the Null Detector at the $L_v$ terminal. The imbalance current vector represents both the magnitude and phase angle difference between $I_x$ and $I_r$. The current is split into 0° and 90° components, amplified, reintegrated, then fed back into the range resistor so that $I_x = I_r$. Because $I_r = I_x$ and $I_r$ flows through $R_r$, the potential at the Low terminal is automatically driven to zero volts—which is why it is also called the virtual ground. The I-V converter output voltage ($V_r$) is represented by the following equation:

$$V_r = I_r R_r = I_x R_r \quad (A.9)$$
Ix is determined by the impedance (Zx) of the DUT and the voltage Vx across the DOT by using equation 2.3, the AC version of Ohm’s law.

From this, we know that the impedance of the DUT (Zx) is:

\[ Z_x = \frac{V_x}{I_x} = R_r \left( \frac{V_x}{V_r} \right) \] (A.10)

The vector voltages Vx and Vr are measured with the vector voltmeters. Since the value of Rr is known, the complex impedance Zx of the DUT can be calculated by using equation A.10. The range resistor determines the impedance measurement range. The Rr value is selected from several range resistors depending on the Zx of the DUT. Due to the vector nature of the voltages, however, the impedance is calculated as shown in

\[ Z_x = \frac{V_x}{I_x} = R_r \frac{V_x}{V_r} = R_r \left[ \frac{a+jb}{c+jd} \right] \] (A.11)

\[ \frac{a+jb}{c+jd} \cdot \frac{c-jd}{c-jd} = \frac{ac-adj+bc-jbdj^2}{c^2-d^2j^2} \] (A.12)

Figure A.6. Vector diagram of Vx and Vr.

Figure A.8 and equations A.11-A.16.
\[
\frac{V_x}{V_r} = \frac{ac + bd}{c^2 + d^2} + j\frac{bc - ad}{c^2 + d^2} \tag{A.13}
\]

\[
Z_x = R_x + jX_x = R_r \frac{V_x}{V_r} \tag{A.14}
\]

\[
R_x = R_r \frac{ac + bd}{c^2 + d^2} \tag{A.15}
\]

\[
X_x = j\frac{bc + ad}{c^2 + d^2} \tag{A.16}
\]

To avoid tracking errors between the two voltmeters, most impedance analyzers measure the \(V_x\) and \(V_r\) with a single vector voltmeter by alternately selecting them. The circuit block, including the input channel selector and the vector voltmeter, is called the vector ratio detector, whose name comes from the function of measuring the vector ratio of \(V_x\) and \(V_r\).

The vector ratio detector measures the ratio of vector voltages across the DUT (\(V_x\)), and across the range resistor (\(V_r\)). The vector ratio detector consists of an input selector switch (ISS), a phase detector, and an analog/digital converter. The measured voltage vectors are used to calculate the complex impedance \(Z_x\) as seen in Figure A.7.

Within the vector ratio detector, the ISS is set to the \(V_x\) position. The phase detector is driven with 0° and 90° reference signals to extract the real and imaginary components (\(a\) and \(jb\) respectively) of the \(V_x\) signal. The A-D converter next to the phase detector outputs digital data for the magnitudes of \(a\) and \(jb\). Next, the ISS is set to the \(V_r\) position. The phase detector and A-D converter perform the same for the \(V_r\) signal to extract the real and imaginary components (\(c\) and \(jd\) respectively) of the \(V_r\) signal.

Once this information is acquired, the other properties are calculated from them. At this low impedance, we are only concerned with series mode model calculations.
\[ DF = \frac{R_s}{\chi_s} = \omega C_s R_s \quad (A.17) \]
\[ C_s = -\frac{1}{\omega \chi_c} \quad (A.18) \]

**A.3.4 RF I-V measurement method**

At higher frequencies (110 MHz to 3 GHz), the RF I-V measurement method is more accurate than the ABB design (up to 110 MHz).

The signal source section generates an RF test signal applied to the DUT within a frequency range from 10 MHz - 3 GHz. The test head section is configured with a current detection transformer, V/I multiplexer, and a test port. The measurement circuit is matched to the characteristic impedance of 50 Ω to ensure optimum accuracy at higher frequencies; the test port also employs a precision coaxial connector of 50 Ω characteristic impedance. Because the measurement circuit impedance is fixed at 50 Ω, all measurements are made in reference to 50 Ω without resorting to use of a range resistor. This allows the instrumental calibration plane to extend to the end of the coaxial connectors.

As we use a home-made probe station, this would normally mean that only correction, not calibration, could be performed. However, while the probe station itself is a non-standard type, the entire electrical pathway has been set up with standardized parts (cables, probe head, probe) which have finely defined electrical parameters which allow the calibration plane to be extended to the tips of the probes.
Since the test current flows through the transformer in series with the DUT, it can be measured from the voltage across the transformer. The V channel signal, Edut, represents the voltage across the DUT and the I channel signal (Etr) represents the current flowing through the DUT.

The vector ratio detector section has a configuration similar to the ABB. The V/I input multiplexer alternately selects the Edut and Etr signals so that the two vector voltages are measured with an identical vector ratio detector to avoid tracking errors. The measuring ratio of the two voltages derives the impedance of the unknown device as

$$Z_x = 50 \times \left( \frac{E_{dut}}{E_{tr}} \right) \quad (A.19)$$
To make the vector measurement easier, the mixer circuit down-converts (in practice, double or triple conversion) the frequency of the Edut and Etr signals to a frequency suitable for the A-D converter's operating speed.
References


Appendix B

Software and Animation.

B.1 E4980a Sample Software Modifications

The Agilent E4980a is provided with a set of sample software written in a variety of languages. While setting up the instrument, I ran into a few limitations on the provided Excel macro software (E4980A_Permittivity_0100.xls), namely: 1. the instrument was capable of reading 201 data points, while the software could only read a maximum of 20. 2. Once the software was changed to read 201 data points, the software began to crash.

These issues were addressed in the following ways:

1. The variable Global Const gNop integer was changed from 20 to 201, setting the maximum number of measurement points.

2. Open Correction: For cnt = 1 to 20, 20 changed to gNop

3. Short Correction: for cnt = 1 to 20, 20 changed to gNop

4. The frequency point column in Excel extended to 201 cells.

5. The frequency point column in Excel filled with a logarithmically calculated 201 data points between 20 Hz and 2 MHz.

6. TimeOutTime value changed from 30000 to 60000 (number of milliseconds the macro runs before timing out)
B.2. Animations for ARPAE 2012 conference

Animations were created for the 2012 ARPAE annual conference. The animations were created in the Hammer map creator provided for free by Valve Software. Both describe how a capacitor is charged and discharged, but from different perspectives—macroscopically and microscopically. These animations may be found in the electronic supplemental for this document.

Animation B1. Effect of frequency on capacitor efficiency.